NASA TECHNICAL MEMORANDUM NASA TM-77457

RESIN COMPOSITION

Masahiro Shiozaki, Nobuya Igarashi, Kiyokazu Tsunawaki

Translation of Japanese Patent No. 51-56849 (1976) to Masahiro Shiozaki, Nobuya Igarashi, Kiyokazu Tsunawaki; Applicant Teijin K.K.; Date of Application, November 13, 1974; Date of Disclosure, May 18, 1976; Japanese Title: Jushi soseibutsu

(NASA-TM-77457) RESIN COMPOSITION (National Aeronautics and Space Administration) 15 p HC A02/MF A01 CSCL 11D

N84-19477

Unclas
G3/24 12470

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, DC 20546 JULY 1982

ORIGINAL PAGE IS
OF POOR QUALITY

STANDARD TITLE PAGE

1. Report No. NASA TM-77457

4. Title and Subtitle

RESIN COMPOSITION

5. Report Date

August 1982

7. Author(s)

Masahiro Shiozaki, Nobuya Igarashi, Kiyokazu Tsunawaki

9. Performing Organization Name and Address

Leo Kanner Associates, Redwood City, California, 94063

11. Contract or Grant No.

NASw- 3541

13. Type of Report and Period Covered

Translation

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration, Washington, D.C. 20546

14. Sponsoring Agency Code

15. Supplementary Notes

Translation of Jushi soseibutsu, Japanese Patent No. 51-56849, Date of application, November 13, 1974, date of disclosure, May 18, 1976.

16. Abstract

The invention relates to an incombustible resin composition produced by blending a compound with a specific ester bond and imido bond in a combustible resin.

18. Distribution Statement

Unclassified - Unlimited

Unclassified

Unclassified

RESIN COMPOSITION

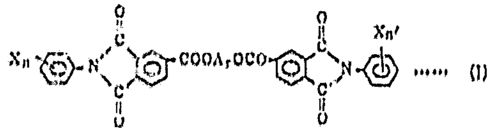
Masahiro Shiozaki, Nobuya Igarashi, Kiyokazu Tsunawaki

1. Title of Invention /287

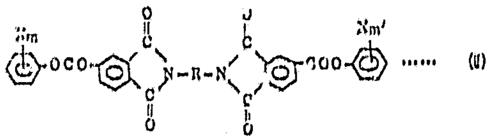
Resin composition.

2. Scope of Patent Claim

The resin composition illustrated in general formula (I) and/or general formula (II)

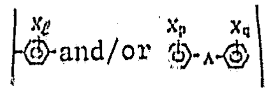


(I)



(II)

characterized by containing the ester imido compound illustrated as follows.

In the formula, Ar represents #1 

(A represents #2 $-C(CH_3)_2-$, $-CH_2-$, $-CH_2CH_2-$, $-SO_2-$, $-S-$ separately or in combination); R represents an alkyl group, cycloalkyl group or allylene group with 2 to 1. arbon atoms (these groups may be substituted by chlorine atoms or bromine atoms); X represents chlorine atoms or bromine atoms; 1, p and q represent integers of 0 to 4; m, m', n and n, represent integers of 1 to 5. These have the relationship of $3 \leq 1 + n + n' \leq 14$, $3 \leq p + q + n + n' \leq 18$ and $3 \leq m + m' \leq 10$.

3. Detailed Description of the Invention

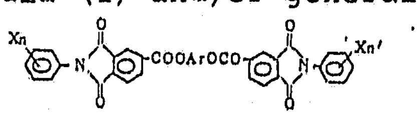
This invention relates to an incombustible resin composition produced by blending a compound with a specific ester bond and imido bond in a combustible resin.

"Numbers in the margin indicate pagination of the foreign text."

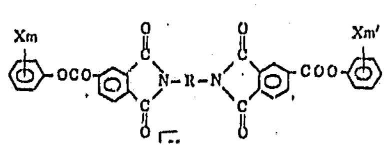
In the past, various halide compounds and phosphorous compounds have been known as fire retardants for combustible resins. The incombustibility of resins has been reduced when resins are heated during molding or heat treatment, for example, due to dispersion of these compounds through evaporation or exudation from resins since many of the compounds have comparatively high vapor pressures. In addition, in the case of halide compounds or phosphorous compounds in which such dispersion is difficult, there are many cases in which the properties of the resin suffer due to dripping during combustion, the formation of color during melting of resin or due to a marked /288 reduction in the ultimate viscosity of the resin in the case of melting of a blend of an ester resin such as polyester or polycarbonate.

The inventors have conducted thorough research into incombustible resin compounds containing fire retardants which undergo virtually no dispersion from the resin, which do not induce adhesion or peeling of resin, which do not drip during combustion and which do not reduce the ultimate viscosity of resin even when contained in ester resins. The discovery that resin compositions containing specific ester imido halide compounds satisfy these requirements completed this invention.

Specifically, this invention is the resin composition illustrated in general formula (I) and/or general formula (II)

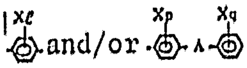
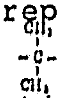


(I)



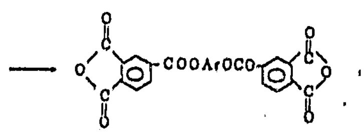
(II)

characterized by containing the ester imido compound illustrated as follows.

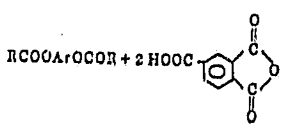
In the formula, Ar represents #3  (A represents #4  , $-CH_2-$, $-CH_2CH_2-$, $-SO_2-$, $-S-$ separately or in combination); R represents an alkyl group, cycloalkyl group or allylene group with 2 to 12 carbon atoms (these groups may be substituted by chlorine atoms or bromine atoms); X represents chlorine atoms or bromine atoms; l, p and q represent integers of 0 to 4; m, m', n and n; represent integers of 1 to 5. These have the relationship of $3 \leqslant l + n + n' \leqslant 14$, $3 \leqslant p + q + n + n' \leqslant 18$ and $3 \leqslant m + m' \leqslant 10$.

Any well-known method of producing the compounds used in the invention and represented by aforementioned general formulas (I) and/or (II) may be used, and various stock compounds may be employed. In the case of the compound illustrated by formula (I), aromatic dihydroxy compounds and trimellitic acid may be reacted by arbitrary method, followed by reaction with aniline. This is illustrated schematically as follows.

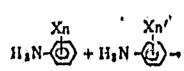
(A) Production of bistrimellitate of diphenol compound.

(1)  (1')

(B represents hydrogen or alkali metal)

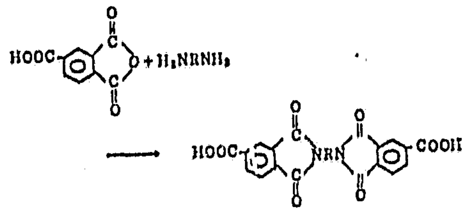
(2)  (1')

(R represents an alkyl group with 2 to 5 carbon atoms)

(B) Compound (I') + #5  compound (I) can be illustrated as an example of production of the ester imido compound illustrated in general formula (I).

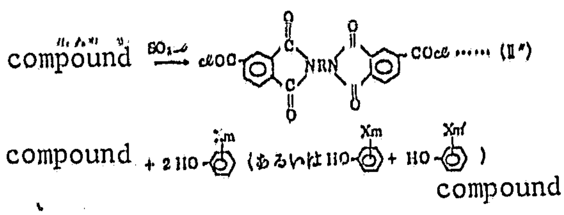
In addition, the compound illustrated in general formula (II) could be produced, for example, by reacting anhydrous trimellitic acid with diamine, forming bisimido dicarboxylic acid which is then reacted with phenol by well-known methods. One example of the method could be illustrated as follows.

(C) First, the production of bisimido dicarboxylic acid from anhydrous trimellitic acid and diamine would be indicated as follows.



(Il')

(D) An example of the production of the compound illustrated in general formula (II) from bisimido dicarboxylic acid and phenol would be indicated as follows.

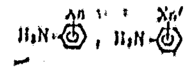


#6 /289

Examples of the aforementioned aromatic dihydroxy compounds would include chloro (or bromo) hydroquinone, 2,5-dichloro (or dibromo) hydroquinone, tetrachloro (or tetrabromo) hydroquinone, 3-chloro (or bromo) resorcin, 2,3-dichloro (or dibromo) resorcin, 3,3',5,5'-tetrachloro (or tetrabromo)-4,4'-dihydroxy diphenol-2,2-bis (3,5-dichloro-4-hydroxyphenol) propane, 2,2-bis (3,5-dibromo-4-hydroxyphenol) propane, bis (3,5-dibromo-4-hydroxyphenol) sulfonate, bis (3,5-dichloro-4-hydroxyphenol) methane, 1,2-bis (3,5-dibromo-4-hydroxyphenol) ethane, and bis (3,5-dibromo-4-hydroxyphenol) sulfide.

Examples of the compounds represented by #7

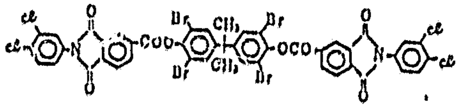
methane, 1,2-bis (3,5-dibromo-4-hydroxyphenol) ethane, and bis (3,5-dibromo-4-hydroxyphenol) sulfide.

Examples of the compounds represented by #7 
would include, O-, p-chloroaniline, O-, p-bromoaniline, 2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-, dichloro (or dibromo) aniline, and 2,4,6-trichloro (or tribromo) aniline.

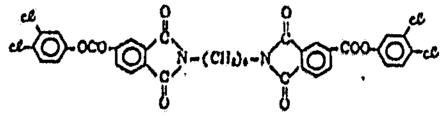
Examples of the aforementioned diamines include ethylene diamine, hexamethylene diamine, dodecamethylene diamine, 1,4-diaminocyclohexane, methaphenylene, paraphenylene diamine, 2,6-diaminonaphthaline, 4,4'-diaminodiphenyl methane, and 4,4'-diaminodiphenyl ether, as well as halogen substitution products of these.

Examples of the aforementioned phenols include 4-bromophenol, 3,4-dibromophenol, 2,4,6-tribromophenol, pentabromophenol, 3,4-dichlorophenol, and pentachlorophenol.

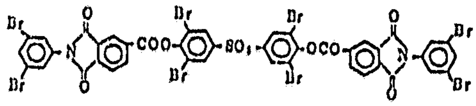
Examples of the compounds illustrated by aforementioned formulas (I) and (II) are as follows.



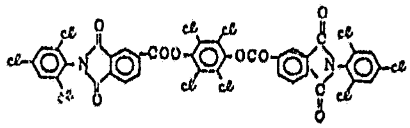
(1)



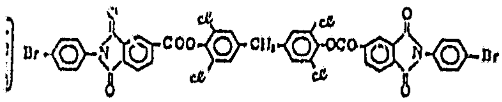
(7)



(2)

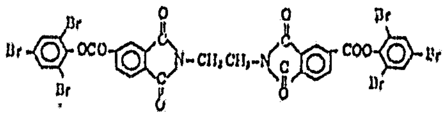


(3)

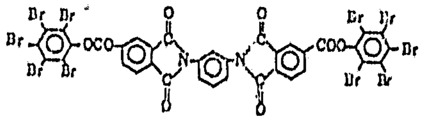


(4)

(1-7).



(5)



(6)

One of these or blends of two or more of these may be blended with combustible resins.

As indicated above, the compounds illustrated in formulas (I) and (II) have a large molecular weight, high melting point, and are stable even when heated above the melting point. For example, the melting point of the compound illustrated in formula (I) with a molecular weight of 1152 is 250°C. No substantial weight reduction is seen until the temperature at which decomposition begins, 394°C, is reached.

The compounds illustrated in aforementioned formula (I) which are produced in this fashion are blended in combustible resins, examples of which include linear saturated aromatic polyesters such as polyethylene terephthalate, polytetramethylene terephthalate, polyhexamethylene terephthalate, polyethylene-2,6-naphthalene dicarboxylate, polytetramethylene-2,6- /290
naphthalenedicarboxylate, polyhexamethylene-4,4'-diphenyl

dicarboxylate, polyethylenediphenoxy ethane-4,4'-dicarboxylate; polyolefins such as polyethylene, polypropylene and polystyrene; polycarbonates derived from diphenols such as bisphenol A, 1,1-bis (4-hydroxyphenyl) cyclohexane; polyacrylate esters such as polymethyl methacrylate; polyamides such as nylon-6, and nylon-6,6; poly (styrene-butadiene) copolymers, ABS resins etc. as well as thermosetting insoluble polyesters such as diallyl phthalate, diallyl terephthalate, and diallyl-2,6-naphthalene dicarboxylate etc.

There is no specific restriction to the methods of blending the fire retardants illustrated by aforementioned general formulas (I) and (II) with these combustible resins. Examples of blending include the method of preblending chips or powder of combustible resin with the aforementioned ester imido compounds illustrated in aforementioned general formula (I) using an extrusion machine, or direct molding of fibers or films, the method involving addition prior to the completion of the production reaction of combustible resins, or the method in which a solution of said resin and said ester imido compound is formed, followed by precipitation of both in a bad solvent, isolation, drying, and molding.

The blending rates of said ester imido compound and combustible resins would vary with the type of combustible resin, the required degree of incombustiblity and the presence of coexisting fire retardants, but in general, 1 to 50 weight parts would be used per 100 weight parts of resin, preferably 5 to 30 weight parts. The molding properties of resin suffer, and the intrinsic properties of the resin are harmed when the amount used exceeds 50 weight parts.

Antimony trioxide as well as oxides of boron, zinc, iron etc. can be added as auxiliary fire retardants to raise the degree of incombustiblity still higher.

In addition, arbitrary additives such as thermal stabilizers or glass fibers etc. may also be blended in the compound of this invention.

The compound of this invention has outstanding incombustiblity, and reduction in the degree of polycondensation of thermoplastic resin as well as reduction in the softening point are not substantially impaired even during fusion. Furthermore, dispersion due to evaporation of the fire retardant substantially does not occur, and the composition has high utility.

Next, this invention is detailed through actual examples. The measurements in the examples are based on "limiting oxygen index (LOI)" as in JIS K 7201-1972.

The UL frame test is the frame test based on Underwriter's Laboratory subsection 94.

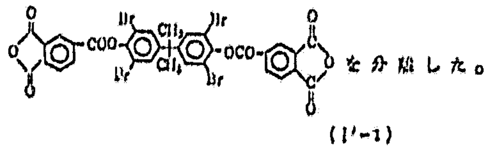
Actual Example 1

This example is one of production of the compounds illustrated in aforementioned general formulas (I) and (II).

[1-1] Aforementioned compound (1)

27.20 g (0.05 moles) of 2,2-bis (3,5-dibromo-4-hydroxyphenyl) propane and 21.05 g (0.10 moles) of 4-chloroformyl anhydrous phthalic acid were introduced into a three neck distillation flask fitted with an agitation apparatus, and 500 ml of 1,1,2,2-tetrachloroethane were added and blended into a homogenous solution, followed by cooling of the entire blend to 5°C. 12 g

of triethylamine were instilled over the course of 30 minutes under agitation. The reaction system became slightly cloudy during instillation. Cooling was terminated after the completion of instillation, and agitation was continued for three hours at room temperature, thereby completing the reaction. 1,1,2,2-tetrachloroethane was distilled off in a bath and removed, followed by the addition of 500 cc of acetone, precipitating triethylamine hydrochloride which was isolated. This was followed by filtration and the introduction of the acetone solution into two liters of water, thereby isolating the following compound.



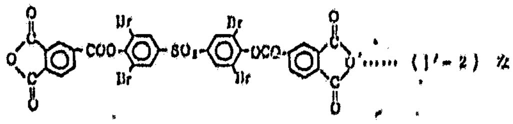
(1'-1)

17.84 g (0.02 moles) of the dried, aforementioned compound (I'-1) and 6.48 g (0.04 moles) of 3,4-dichloroaniline were introduced into a three neck distillation flask fitted with an agitation apparatus followed by the introduction of 200 ml of diethylene glycol, dimethyl ether and 25 ml of metaxylene. The temperature of the system was maintained at 150°C under agitation, and the reaction was conducted for 10 hours while the water generated was boiled with m-xylene and expelled. Subsequently, approximately 100 ml of diethyleneglycol dimethylether were distilled off at reduced pressure and removed. Upon cooling of the system, pale yellow crystals precipitated. These crystals were confirmed to be aforementioned compound (I) from the infra-red spectrum. The results of differential thermal analysis revealed the melting point to be 250°C and the temperature at which decomposition begins to be 394°C. /291

[1-2] Aforementioned compound (2)

28.30 g (0.05 moles) of bis (3,5-dibromo-4-hydroxyphenyl) sulfonic acid, 4.2 g (0.105 moles) of caustic soda and 300 ml of

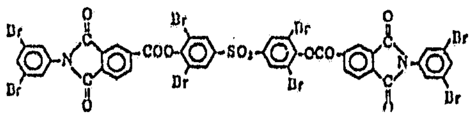
N,N-dimethyl acetoamide were introduced into a one liter three neck distillation flask fitted with an agitation apparatus and reacted for approximately two hours at 80°C, whereupon all of the bis (3,5-dibromo-4-hydroxyphenyl) sulfonic acid turned into sodium salt. This was dissolved in N,N-dimethylacetoamide. A solution in which 21.05 g (0.10 moles) of 4-chloroformyl anhydrous phthalic acid were dissolved in 50 ml of N,N-dimethylacetoamide was instilled over the course of 30 minutes. After the completion of instillation, the temperature was raised to 180°C and the reaction was conducted at that temperature for three hours. The system subsequently was cooled to approximately 110°C and then added to two liters of water, whereupon the compound illustrated below



(1'-2)

precipitated and was isolated. This was filtered and dried.

The compound illustrated below

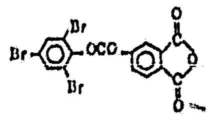


(2)

was produced following imide formation by the method explained in aforementioned section [1-1] using 18.28 g of the aforementioned compound [I'-2] and 10.04 g of 3,5-dibromo aniline. The results of differential thermal analysis revealed the melting point to be 262°C and the temperature at which decomposition begins to be 372°C.

[1-3] Example of production of the compound illustrated in aforementioned formula (5)

33.08 g (0.57 moles) of 2,4,6-tribromophenol, 21.07 g (0.1 mole) of 4-chloroformyl anhydrous phthalic acid and 300 ml of tetrahydrofuran (THF) were introduced into a one liter three neck distillation flask fitted with an agitation apparatus, and a solution in which 12 g of triethylamine were dissolved in 50 ml of THF was instilled over the course of 30 minutes while the entire system was maintained at 5°C. Agitation was continued for three hours at that temperature. Subsequently, the entire system was introduced into three liters of water and the resulting precipitate was isolated by filtration. It was thoroughly washed with water at approximately 40°C and dried. The total weight of the material was 47.50 g. Infrared spectral analysis revealed it to be derived from 2,4,6-tribromophenol. The compound was identified as follows.



#8

25.2 g (0.05 moles) of this compound, 1.50 g (0.025 moles) of ethylene diamine and 100 ml of N-methyl-2-pyrrolidone were introduced into a 300 ml volume three neck distillation flask and agitated for three hours at 25°C, followed by the addition of 50 ml of toluene. The entire system was then heated to 140°C and the water generated was expelled from the system. In addition, the toluene was distilled off and removed. The operation took four hours. Subsequently, the system was introduced into two liters of water and the resulting precipitate was washed with THF. Infrared spectral analysis of the material revealed it to be the compound of formula (5).

Actual Examples 2-5 and Comparative Examples 1-3 /292

Fire retardants and antimony oxide were blended into 100 weight parts of resin in the proportions illustrated in table 1

and molten blending was conducted using extruders. After formation of chips, test pieces were molded using an injection molding device. The sublimation properties during molding of the test pieces and the results of combustion of the test pieces are as illustrated in table 1.

Table 1

1 実施例	2 難燃剤	3 対象ポリマー (100重量部)	4 難燃剤量 (重量部)	5 三酸化アンチモン (重量部)	LOI	6 滴下性*	7 成形時の昇華**
2	(1)	ポリエチレンテレフタレート 8	15	5	30	○	○
3	(2)	ポリテトラメチレンテレフタレート 9	6	2.1	31	○	○
4	(1)	6−ナイロン 10	6	24	29	○	○
5	(3)	ポリエチレンテレフタレート 11	10	3	28.5	○	○
12 比較例1	13 ヘキサブロモベンゼン	ポリエチレンテレフタレート 14	12	5	31	△	×
2	テトラブロモ無水フタル酸 15	同上 16	11	5	29	×	×
3	テトラブロモビスフェノールA 17	ポリテトラメチレンテレフタレート 18	15	5	27	×	×
4	無 19	ポリエチレンテレフタレート 20	0	0	24	×	—

21 * 滴下性 ○印 燃焼時殆んど滴下なし
×印 滴下あり

22 ** 成形時の昇華 ○印 なし
×印 有

1 actual example
2 fire retardant
3 object polymer (100 weight parts)
4 amount of fire retardant (wt. parts)
5 antimony trioxide (weight parts)
6 dripping properties *
7 sublimation during molding **
8 polyethylene terephthalate
9 polytetramethylene terephthalate
10 6-nylon
11 polyethylene terephthalate
12 comparative example 1
13 hexabromobenzene
14 polyethylene terephthalate
15 tetrabromo anhydrous phthalic acid
16 same as above
17 tetrabromo bisphenol A
18 polytetramethylene terephthalate
19 none
20 polyethylene terephthalate
21 * dripping properties O virtually no dripping during combustion
x dripping occurred
22 ** sublimation during molding O symbol absent
x symbol present

The composition of this invention exhibits outstanding incombustiblity based on the results in table 1, and no dripping during combustion nor sublimation during molding occur in comparison to the case of use of conventional fire retardants. Thus, the superiority of this composition is evident. /293

Actual Example 6

95 weight parts of commercial diallyl phthalate prepolymer, 5 weight parts of diallylate terephthalate monomer, 15 weight parts of fire retardant (1), 2 parts of t-butyl perbenzoate, 5 weight parts of antimony trioxide, 100 weight parts of calcium carbonate and 50 weight parts of glass fibers of 1/8 inch length were thoroughly blended at 100°C, and test samples were produced through compression molding for three minutes under pressure of 50 kg/cm^2 at 1,600°C. Combustion tests were conducted using the test samples, with an LOI of 36.0, while in UL flame tests, the after-glow lasted for 8.7 seconds and there was no dripping. The material was ranked at 94 V-O.